



Adsorption of 2,4,6-trichlorophenol on kaolinite: DFT calculations

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Abstract – The aim of this work is to explore the adsorption process of an organic pollutant the 2,4,6-trichlorophenol on the clay mineral (kaolinite) surface in order to identify the sites of adsorption as well as conformations corresponding to the lowest energies. Ab-initio calculations have been used to investigate the adsorption process using a representative cluster model. According to the results obtained on the various studied models, the orientations of TCP on the surfaces clay affect the parameters such as: HOMO-LUMO energy gap, the enthalpy change, the thermal Gibbs free energy and entropy contribution. The results point out a preferential adsorption of TCP on the octahedral surface and the NBO analysis indicates that the electron donor-acceptor complex was the dominant adsorption mechanism.

Key words: Adsorption; 2,4,6-trichlorophenol; kaolinite; cluster; DFT calculations

Introduction

The clay minerals, as natural materials, are among the world's most important and useful industrial minerals. They are used in traditional and industrial applications and because of their high surface areas, they are often used as adsorbents (Patwardhan and Clarson, 2002; Savin and Lee, 1988; Tunney and Detellier, 1996; Komori *et al.*, 1998; Guimaraes *et al.*, 1998; Ogawa and Kuroda, 1995) especially for organic compounds coming from different sources: industry, agriculture, chemical warfare and home products.

Phenol and its derivatives are among the most frequent contaminants of water, they are widely used as intermediates in the synthesis of dyes, pesticides, insecticides, explosives, etc. (Salvador and Merchan, 1996).

We have chosen for our study the 2,4,6-trichlorophenol (TCP) molecule because it is one of the most wide-spread pollutants in the environment. It is recognized as a toxic carcinogen (Podkoscielny *et al.*, 2003), and is also a weak acid which can easily permeate into the human skin in vitro and is readily absorbed by the gastro-intestinal tract (Hameed *et al.*, 2009); It is normally found in the industrial wastewater such as from paint, pharmaceutical, pesticide, wood, pulp and paper industries as well as water disinfecting process (Hameed, 2007; Gao and Wang 2007). The TCP was listed by the Environmental Protection Agency (EPA) as one of 31 high-priority pollutants, appearing on the EPA's "persistent, bio-accumulative and toxic" (PBT) chemicals list (EPA, 1980; EPA, 2002).

The stable carbon-chlorine bond and the position of chlorine atoms relative to the hydroxyl group are responsible for their toxicity, carcinogenic properties, structural stabilization and persistence in the environment, making the removal of the TCP from the environment very crucial (Vidic *et al.*, 1993). Waste waters containing such phenolic compounds must be treated before being discharged (Oh *et al.*, 2003) and degradation of these substances means the appearance of phenol and its derivatives in the environment (Dabrowski *et al.*, 2005).

The aim of this study is to understand the adsorption process of 2,4,6- trichlorophenol (TCP) on the kaolinite surface. This pollutant was widely investigated experimentally (Hameed, 2007; Gao and Wang, 2007; Chaliha and Bhattacharyya 2008; Tan *et al.*, 2009) since it is one of the most widespread pollutants in the environment but to our knowledge, no investigations involving a theoretical study of the interactions of TCP with clay minerals have been performed.

Materials and Methods

The study of the adsorption of TCP on kaolinite layers was performed using the density functional theory with the Becke's three parameter exchange functional (Becke, 1993) with the Lee-Yang-Parr nonlocal correlation functional (B3LYP). The 6-31G** basis set was applied and the GAUSSIAN-09 program package (Frisch, 2009) was used in this study. The starting geometry of TCP was taken from the published X-ray data (González *et al.*, 2007).

For our investigation we used a cluster of clay mineral as most of the theoretical studies of the interactions between clay minerals and the organic species apply cluster approximations, which prove to be very useful for giving detailed insight concerning the adsorption processes of organic molecules on clay minerals. We have modelled the adsorption of TCP on the tetrahedral and octahedral side of the kaolinite. Minerals of the kaolinite group have a common chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and the most common are kaolinite and dickite. Kaolinite is a layered aluminosilicate mineral affiliated to the class of dioctahedral 1:1 clay.

Individual kaolinite layers consist of an octahedral aluminum hydroxide sheet and a tetrahedral silicate sheet interconnected via the plane of apical oxygen atoms. One side (octahedral) of the kaolinite layer is covered with the surface hydroxyl group while the opposite side (tetrahedral) is formed from basal oxygen atoms of the tetrahedral sheet.

The structure of TCP was minimized with the B3LYP method at 6-31G* level and its position with respect to the surface cluster was fully optimized. The representative cluster models of the tetrahedral and octahedral surface of kaolinite were constructed using its structural data (Bish, 1993) whose chemical formula is $\text{Si}_6\text{Al}_6\text{O}_{36}\text{H}_{30}$ and was constructed as a cut out from the periodic structure. Dangling bonds of the mineral-layer fragment was saturated with hydrogen atoms.

The model of kaolinite used to simulate the adsorption on the tetrahedral and octahedral surface consist of one tetrahedral and one octahedral ring respectively. The regular layer surfaces are parallel to the (001) plane. The isolated layers are identical and are formed from one ditrigonal silicon-oxygen ring of tetrahedral sheet and one aluminium-oxygen ring of octahedral sheet. Both sheets share a common plane of apical oxygen atoms. The isolated kaolinite layer is electroneutral so the interlayer space is empty and no compensating cations are required. Such models have been used in various investigations (Song *et al.*, 2013 ; Scott *et al.*, 2014 ; Wang *et al.*, 2013 ; Robinson *et al.*, 2007 ; Michalkova and Tunega, 2007). The surface of the octahedral sheet is covered with surface hydroxyl groups, which are involved in hydrogen bonds with basal oxygen atoms of the adjacent layer. The structure of this cluster is displayed in figure 1.

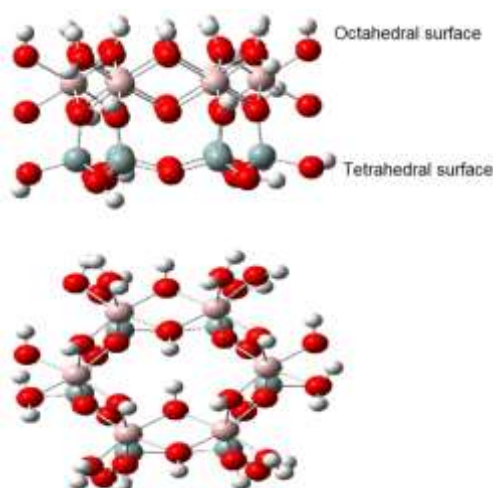


Figure 1. Two views of the of kaolinite cluster model

Computational details

Studies of adsorption of trichlorophenol on a kaolinite cluster have been performed within the density functional theory (DFT) as implemented in Gaussian 09 package. Full geometry optimizations were carried out in gas phase for all structures under investigation. All of them were identified as minima by means of a harmonic vibrational analysis. The location of the adsorbate on the surface of the kaolinite layer is governed by the shape of the electrostatic potential and its ability to form attractive contacts with the surface of clay the reason for which we created several models for adsorption of TCP on the tetrahedral and octahedral side of the kaolinite, which differ by the position of the studied molecule on the cluster surface and we approached on every case the following parameters: binding energy, enthalpy, the thermal Gibbs free energy, constant of reaction and NBO analysis. We noticed, for the various studied cases, the formation of several hydrogen bonds.

The TCP molecule was placed above the octahedral hole of kaolinite in such a way that hydroxyl group of the TCP is directed into the center of the octahedral cavity while for the tetrahedral sheet, the molecule of TCP was located in parallel and perpendicular to the surface clay. The starting geometries and final optimized structures of adsorbed complexes are shown in figures 2 and 3.

Calculations are presented for HOMO-LUMO energies, the binding energies corrected to the BSSE, Boys–Bernardi's counterpoise procedure (CP) was used to calculate the basis set superposition errors (BSSE) (Boys and Bernardi, 1970). To investigate the thermodynamics of the binding process, the thermodynamic calculations were carried out by B3LYP/6-31G**. The enthalpy change (ΔH), the thermal Gibbs free energy (ΔG), entropy contribution (ΔS) and adsorption constant, for all adsorbed configuration was obtained. The NBO analysis of hydrogen bonded systems was calculated and the strength of this interaction was estimated by the second order perturbation theory.

Binding energy of TCP adsorbed on the kaolinite is computed using the following equation.

$$BE_{bin} = E_{Tot(TCP/kaolinite)} - E_{(TCP)} - E_{(kaolinite)} \quad (1)$$

Where BE_{bin} is the binding energy of the adsorbed molecule to the kaolinite sheet. E_{Tot} is the total energy of the system, E_{TCP} and $E_{kaolinite}$ are those of the isolated molecule and isolated kaolinite, respectively. By the definition, a negative value of BE_{bin} corresponds to exothermic adsorption. The adsorption constant K at 298K and 1 atm is computed using a thermodynamic equation.

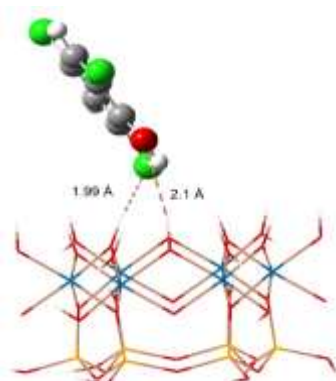
$$\Delta G^\circ = - RT \ln k \quad (2)$$

Results and Discussion

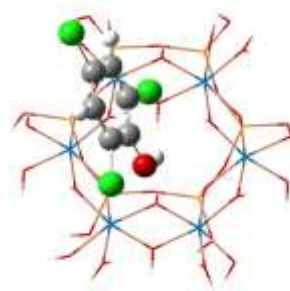
Geometry optimization

In order to obtain the stable configurations of the TCP adsorbed on the kaolinite sheet, various possible initial adsorption geometries are considered where the molecule is oriented perpendicular, parallel and in an oblique position in such a way that the oxygen atom of the TCP is in the role of the proton acceptor and/or donor with protons from surface hydroxyl groups on the octahedral and tetrahedral side of the kaolinite layer, see initial structures on figure 2. On this figure, the separating distances of the hydroxyl group and chlorine atom of the TCP molecule to the closest hydroxyl groups of kaolinite layer surface are represented.

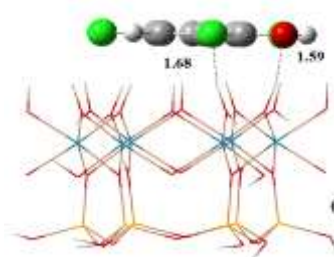
Structures of all models optimized with B3LYP/ 6-31G** level are illustrated in figure 3. For better description, two views are represented for each model. As shown in Fig 3, the TCP is adsorbed on the surface cluster through several different types of hydrogen bonds; structural data of these intermolecular bonds occurring in adsorbed systems are collected in table 1.



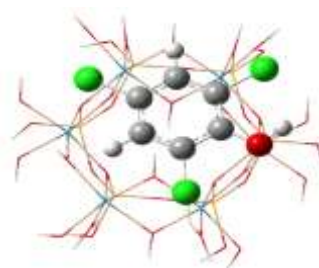
(A1)



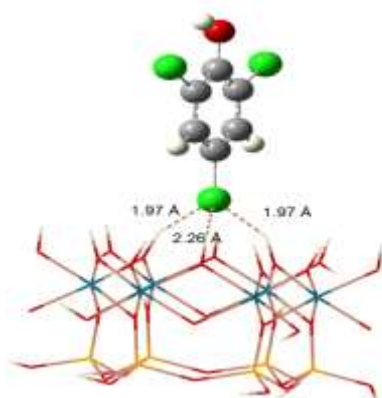
(A2)



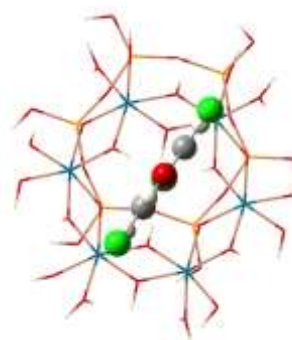
(B1)



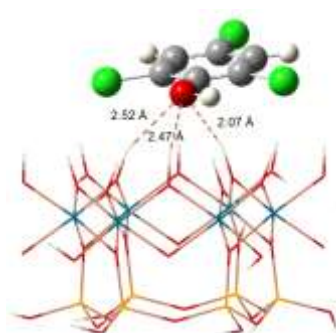
(B2)



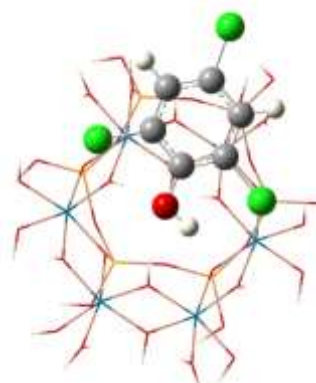
(C1)



(C2)



(D1)



(D2)

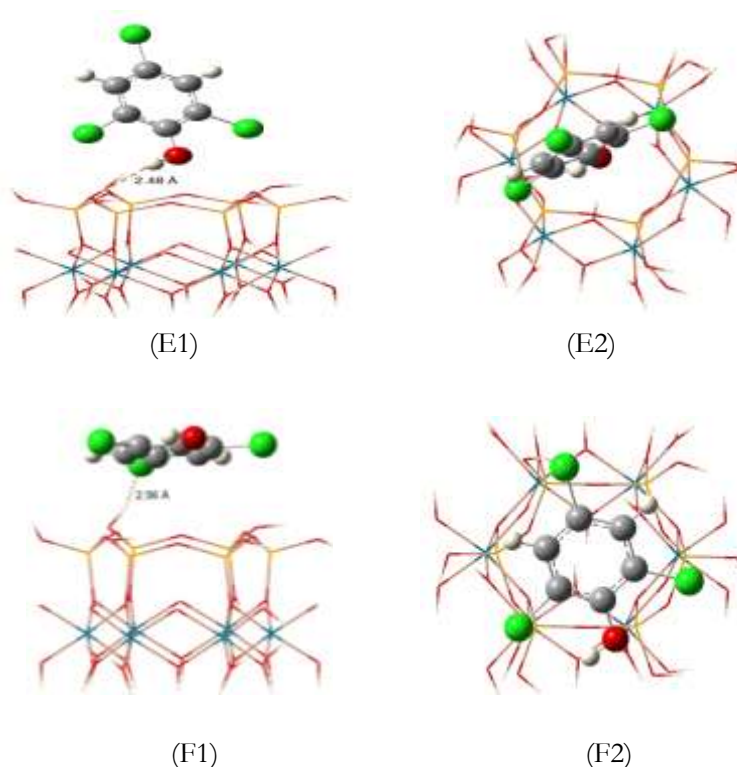


Figure 2. Initial geometrical structures of TCP-kaolinite complex on: octahedral sheet of kaolinite (A-B-C-D) configurations and tetrahedral sheet of kaolinite (E-F) configurations. (Right) Top and (left) front views. Atom colours are Blue: Al, Yellow: Si, Red: O, Green: Cl, White: H and Grey: C.

Table 1. Hydrogen Bond length calculated with B3LYP/6-31g** in TCP-kaolinite complex.

Configuration	Number of hydrogen bond	Hydrogen bond	Bond length (Å)
<u>Octahedral surface</u>			
(A)	4	C ₂ —Cl ₇ ---H ₆₃ —O ₄₆	2.80
		C ₂ —Cl ₇ ---H ₆₆ —O ₄₈	2.56
		C ₆ —Cl ₉ ---H ₂₃ —O ₁₇	2.56
		O ₁₀ —H ₁₁ ---O ₁₈ —H ₂₄	1.62
(B)	4	C ₂ —Cl ₇ ---H ₆₃ —O ₄₆	2.80
		C ₂ —Cl ₇ ---H ₆₆ —O ₄₈	2.56
		C ₆ —Cl ₉ ---H ₂₃ —O ₁₇	2.55
		O ₁₀ —H ₁₁ ---O ₁₈ —H ₂₄	1.62
(C)	1	C ₄ —Cl ₈ ---H ₂₅ —O ₁₉	2.62
(D)	2	C ₂ —Cl ₇ ---H ₂₁ —O ₁₅	2.92
		O ₁₀ —H ₁₁ ---O ₁₇ —H ₂₃	1.54
<u>Tetrahedral surface</u>			
(E)	1	<div><div>C₁—O₁₀—H₁₁---</div><div>O₃₁<^{Si₃₀_{Si₃₂}}</div></div>	2.24
(F)	/	/	/

We have retained four configurations for the position of TCP above the octahedral surface:

Configuration (A): Figure 3 illustrate the optimized geometries of the TCP-kaolinite system with TCP placed in a perpendicular orientation toward the surface. From the top view of the geometry we can see the hexagon of the TCP molecule centred a hexagon of the kaolinite cluster, the oblique orientation is

maintained. Hydroxyl group and two chlorine atoms of TCP are oriented toward the surface sheet above the octahedral hole. Four hydroxyl groups, which are surrounding the hole in the octahedral sheet, are involved in hydrogen bonding with the absorbance of TCP molecule. Three of them act as protons donors to the TCP chlorine atoms and the fourth one act as proton acceptor for the proton of hydroxyl group of the TCP molecule at O...H distance about 1.62 Å.

Configuration (B): Initially the molecule cantered the hole of the layer sheet and was oriented in a parallel way toward the octahedral surface; after optimization configuration (B) has led to the same structure as revealed from the optimization of configuration (A). Adsorption of the TCP molecule on these two models is governed by the same hydrogen bonds. We notice once again the bi-functional ability of the surface hydroxyl groups, which can act either as proton donor or as proton acceptor.

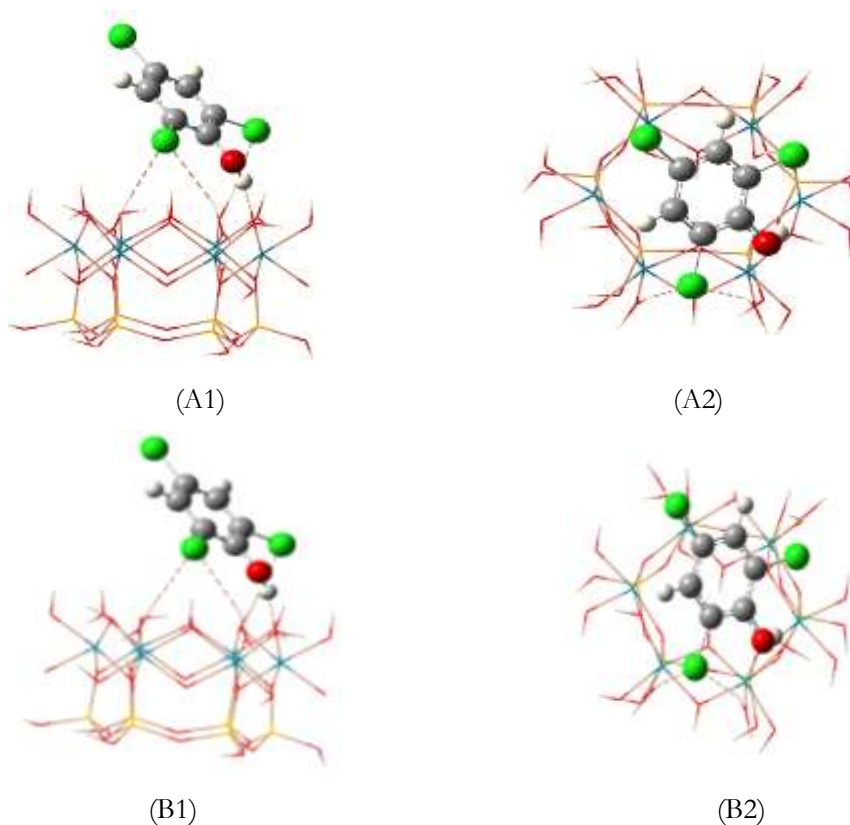
Configuration (C): In this case, the hydroxyl group of the TCP was oriented perpendicular and in the opposite direction of surface sheet. After optimization, in addition to being tilted up at few degrees from the initial position, the molecule has been rotated roughly 60° around an axis perpendicularly to the molecule plan. The chlorine atom is bounded to hydroxyl groups of the surface sheet as proton acceptor.

Configuration (D): initially the TCP molecule is oriented in oblique position; the oxygen atom is bonded to three hydroxyl groups of the surface layer. After optimization of the structure, two hydroxyl groups of the surface sheet were involved in hydrogen bonding with the absorbance molecule as donor and acceptor of proton in a distance between 2.92 and 1.54 Å, respectively which is the smallest distance obtained between the TCP molecule and the octahedral surface of kaolinite.

For the tetrahedral side two configurations were retained:

Configuration (E): initially the TCP molecule was oriented perpendicularly to the surface layer; this position was maintained after optimization. There is formation of a single intermolecular hydrogen bond between the phenol hydroxyl group and the oxygen atom of the tetrahedral surface. The corresponding interaction distance is about 2.24 Å

Configuration (F): the TCP molecule was positioned in a parallel orientation with the hexagon of the molecule on top of the surface layer, after optimization this position was maintained with nevertheless a light rotation of some degrees. No intermolecular hydrogen bond has been formed.



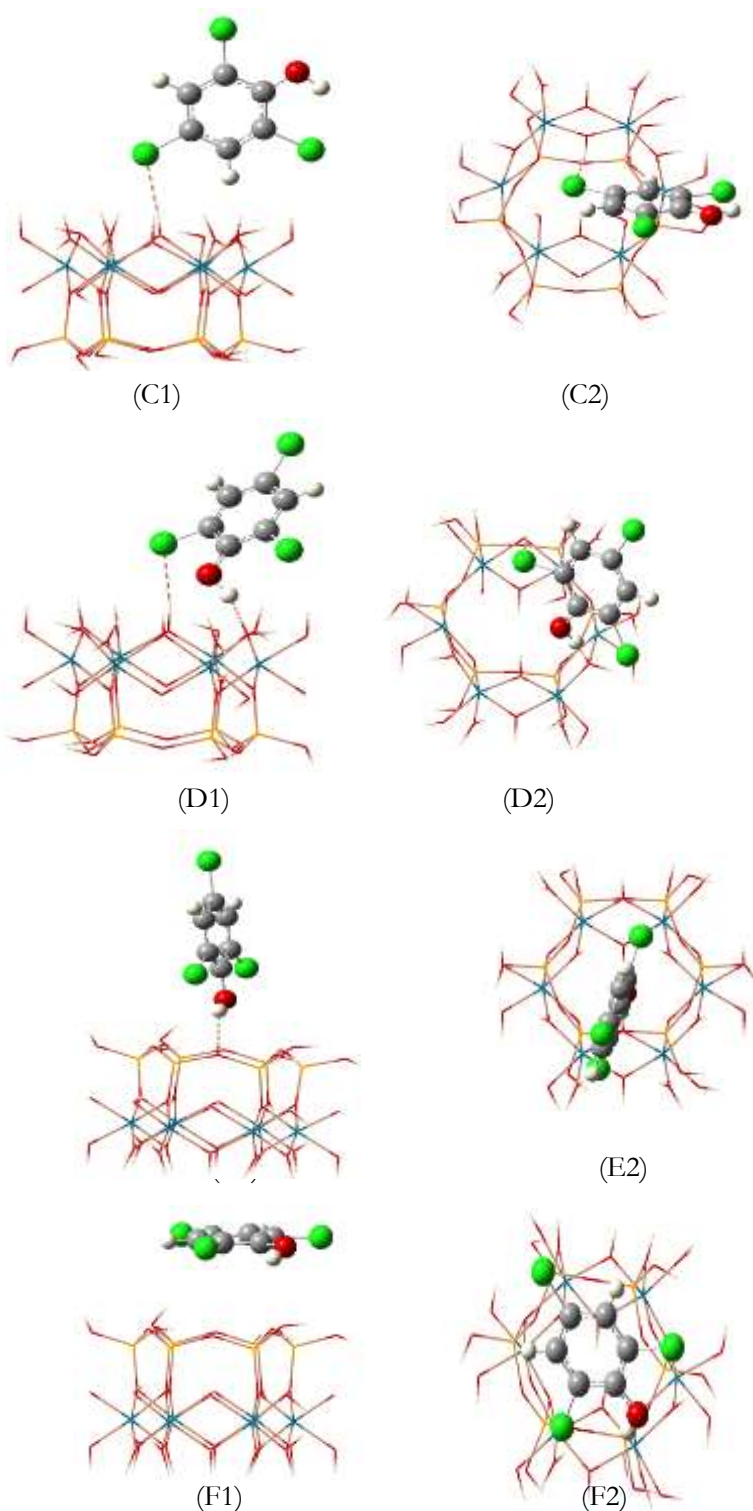


Figure 3. Optimized structures of TCP- kaolinite complex with B3LYP/6-31G**. Octahedral sheet of kaolinite (A-B-C-D) configurations and tetrahedral sheet of kaolinite (E-F) configurations. (Right) Top and (left) front views. Atom colors are Blue: Al, Yellow: Si, Red: O, Green: Cl, White: H and Grey: C.

Binding energy

The results summarized in table 2 for the most stable structures shows the calculated binding energy (BE) of the TCP interaction with kaolinite, BSSE with conventional counterpoise (CP) method, real BSSE corrected binding energies and the relative energy difference of all studied systems.

From the BSSE values calculated with the counterpoise method (CP) we notice that our results are in good agreement with the results of Michalkova (Michalkova *et al.*, 2011). The CP procedure most likely overestimates the BSSE the reason for which previous studies (Wang *et al.*, 2013; Austen *et al.*, 2008; Sainz-Díaz *et al.*, 2011) have suggested that, for systems with weak interactions, the real BSSE is small and the real BSSE can be considered to be one order of magnitude lower than that calculated by the counter-poise (CP) method ($BSSE = CP/10$) proposed by Austen et al (Austen *et al.*, 2008). In this paper, we applied the approximation of $BSSE = CP/10$.

Table 2. Binding energy (BE_{bin}), relative energy difference, BSSE with conventional counterpoise (CP) method ($BSSE_{CP}$) and real BSSE corrected binding energies ($BE_{bin\text{ Corr}}$) of all studied systems calculates at B3LYP/6-31g**.

n	Configuratio	BE_{bin} (kcal/mol)	ΔE	$BSSE_{CP}$ (kcal/mol)	$BE_{bin\text{ Corr}}$ (kcal/mol)
Octahedral Surface					
	(A)	-17.257	1.574	5.194	-16.738
	(B)	-17.259	1.572	5.198	-16.739
	(C)	-5.805	13.026	3.152	-5.489
	(D)	-18.831	-	5.589	-18.272
Tetrahedral surface					
	(E)	-7.790	-	4.825	-7.308
	(F)	-7.039	0.751	5.069	-6.532

The negative binding energy proves that the TCP can form stable complexes with kaolinite. The BSSE corrected binding energies are within a range of -5.489 to -18.272kcal/mol for the octahedral surface. Relative stabilities of the adsorption complexes structures based on their relative binding energies are in order: configuration (D) > (A) \approx (B) > (C) for the octahedral surface, (A) and (B) configurations showed binding energies of the same order of magnitude.

The interaction energies amount to about -16.7 kcal mol⁻¹. In these two configurations the molecule was placed initially directly above the center of the octahedral cavity in perpendicular and in parallel (after optimization this orientation changes to perpendicular) to the plane of the surface hydroxyl groups, in a range of sizes from 1.99 to 2.1 Å and from 1.59 to 1.68Å, respectively, see figure 2. Configuration (D) offers the energetically most predisposed position to an adsorbate molecule, the $BE_{bin\text{ Corr}}$ value is -18.272 kcal/mol. The average distance of the intermolecular bond for (A) and (B) configurations is 2.38Å which is longer than 2.23 Å on configuration (D). It should be mentioned that for these two configurations, the formation and the co-operation of the multiple H-bonds with the surface hydroxyl groups surrounding the hole in the octahedral surface affect the adsorption energies. These hydrogen bonds are formed due to the flexibility of the surface hydroxyl groups. For the tetrahedral surface, based on their relative binding energies, configurations are in order (E) > (F) with the values of -7.308 and -6.532 kcal/mol respectively. Configuration (E) is more favourable than (F) configuration by an energy difference of 0.751 kcal/mol.

The Configuration (C) shows a weak interaction, $BE_{bin\text{ corr}}$ value is about -5,489kcal/mol, which is much less than the interaction energies on the tetrahedral surface we assume that has a relationship with the fact that the adsorbate is not linked to the octahedral surface with his OH group. In this configuration, the TCP molecule was bonded to the surface sheet with its chlorine atom Cl_s. The data reported in table 2 indicate also that greater adsorption energies are observed for the octahedral surface than the tetrahedral one with the energy difference of about 11kcal/mol. This result is in accordance with conclusions of previous studies (Castro *et al.*, 2012; Boys and Bernardi, 1970; Michalkova *et al.*, 2011). This suggests that TCP molecule is much more stabilized on the octahedral kaolinite surface due to the formation of multiple hydrogen bonds between the TCP molecule and the hydroxyls surface. However if we compares between the configurations (D), (A) and (B) we have to note that configuration (D) has only 2 hydrogen bonds but are significantly more stable than configuration (A) and (B) which have four H-bonds. Three of them are C-Cl ...H hydrogen bonds and are characterized as weak with distances in the 2.55-2.80 Å interval. From the length of the

hydrogen bonds listed in Table1 we can see that the shortest bonds precisely corresponds to the configuration (D) with 1.54 Å ; this leads to conclusion that the shorter the hydrogen bond length is, the more stable the interaction is.

Thermochemistry

The Calculated thermodynamic values are presented in Table 3. The negative ΔG° values obtained for configurations (A), (B) and (D) indicate the feasibility and spontaneous nature of TCP adsorption. The negative values of ΔH° and ΔS° , in all cases, indicate that the adsorption process is exothermic and an enthalpy-driven process. Furthermore, the absolute values of ΔH° are increasing in the order of (C) < (A) \approx (B) < (D), suggesting a higher affinity for the configuration (D). However the enthalpy changes for the octahedral sheet is more negative than on the tetrahedral side. This corresponds with the strength of intermolecular binding.

Unfortunately, we did not find any relevant experimental thermochemical data for the TCP-kaolinite intercalation process to compare with our theoretical investigations.

All adsorption reactions of the studied complexes are spontaneous, except the adsorption process of the configuration (C), (E) and (F) see table 3. The adsorption coefficients for these adsorption processes has a value of $5.99 \cdot 10^{-4}$ for configuration (C), $1.24 \cdot 10^{-2}$ and $8.63 \cdot 10^{-4}$ for configuration (E) and (F), respectively, implying that binding interaction are not favored.

The adsorption coefficient is more important with configuration (D) with a value of $4.38 \cdot 10^9$. ΔS° value indicates that the adsorbate is weakly bound, likely by Van der Waals forces to the surface clay.

Table 3. Thermodynamics properties, adsorption constants for all configurations of adsorption processes

Configuration	ΔH°_{298} (kcal/mol)	ΔG°_{298} (k cal/mol)	ΔS°_{298} (kcal/mol.K)	K_{298}
Octa hedral surface				
(A)	-15.81	-4.30	-0.0385	$1.38 \cdot 10^3$
(B)	-15.82	-4.31	-0.0386	$1.38 \cdot 10^3$
(C)	-4.74	4.42	-0.0307	$5.99 \cdot 10^{-4}$
(D)	-23.72	-13.23	-0.0351	$4.38 \cdot 10^9$
Tetrahedral surface				
(E)	-6.38	2.61	-0.0301	$1.24 \cdot 10^{-2}$
(F)	5.70	4.20	-0.0332	$8.63 \cdot 10^{-4}$

Homo–Lumo Gap

The lowest unoccupied molecular orbital energies (E_{LUMO}) witch characterizes the ability of electron accepting, the highest occupied molecular energies (E_{HOMO}) witch characterizes the ability of electron giving and energy gaps ($\Delta E_{\text{HOMO-LUMO}}$) of all adsorption complexes are shown in table 4. These values inform us about the relative reactivity of the TCP adsorbed on the kaolinite and the molecular chemical stability. Chemicals with larger ($\Delta E_{\text{HOMO-LUMO}}$) values tend to have higher stability (Karelson *et al.*, 1996). The results reported in table 4, for the energy gap agree well with the results of the binding energies. The relative reactivity's of the TCP adsorbed on kaolinite are in order: configuration (D) > (A) \approx (B) > (C) what mean that configuration (D) have higher stability due to the large energy gap and configuration (C) is a soft molecule due to small energy gap.

However for tetrahedral sheet we noticed HOMO level slightly move to lower energies so ΔE of the configuration decreased to 0,824 eV for configuration (E) and 0,779 eV for configuration (F). The small band gap values reflect the lower stability of the adsorption process for the tetrahedral sheet.

Table 4. The lowest unoccupied molecular orbital energies (E_{LUMO}), the highest occupied molecular orbital energies (E_{HOMO}) and frontier molecular orbital energy gap ($\Delta E_{\text{HOMO-LUMO}}$) of all studied systems

Configuration	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE(HOMO-LUMO) (eV)
Octahedral surface			
(A)	-4.297	-2.246	2.051
(B)	-4.128	-2.158	2.050
(C)	-3.911	-2.140	1.771
(D)	-4.156	-2.002	2.154
Tetrahedral surface			
(E)	-3.313	-2.489	0.824
(F)	-3.262	-2.483	0.779

NBO analysis

NBO analysis was undertaken to estimate the role of intermolecular charge transfer in determining the strength and equilibrium length of the hydrogen bond in the studied complexes. The donor–acceptor interactions of the TCP adsorption on the kaolinite clay surface were illustrated in Table 5

According to the NBO results, the TCP molecule intervenes as donor with chlorine Cl₇ for configuration A, B, D this hydrogen bond seems to be the weakest one since it is the longer than the others H-bonds; TCP molecule intervenes also as donor with Cl₈ in the configuration (C) and with Cl₉ in configuration (A). Whereas the kaolinite cluster intervenes as donor with the oxygen of the hydroxyl groups: O₁₈ for the configuration (A) and (B), O₁₇ for configuration (D) and O₃₁ for configuration (F).

Table 5 lists the calculated second order interaction energy E⁽²⁾ values between donor–acceptor orbitals in the studied configurations. The magnitude of charges transferred from a lone pair oxygen atom, LP O17 to the anti-bonding acceptor σ* O10 - H11 shows that stabilization energy of about 40.55 kcal/ leads to the weakening of the H-bond corresponding to a bond length of 1.54 Å.

When the kaolinite acts as a donor, the energy stabilization is much larger than when TCP acts as donor.

We have to note that when the kaolinite plays the role of donor, the important intermolecular hydrogen bond is observed between LP O 18 and σ* O10 - H11 with energy equal to 9.45 and 9.37 kcal/mol for configuration (A) and (B) respectively as well as for the H-bond observed between LP O17 and σ* O10 - H11 with an energy about 40.55 kcal/mol.

Table 5. Donor-acceptor interactions energies, distances and angles obtained for all studied systems calculate at B3LYP/6-31g**.

Donor	Acceptor	E ⁽²⁾ (k(kcal/mol)	Bond length A	Angle (°)
Octahedral surface				
Configuration (B)				
LP Cl 7	σ* O 46 - H 63	0.25	2.80	159.43
LP Cl 7	σ* O 48 - H 66	4.37	2.56	174.13
LP Cl 9	σ* O 17 - H 23	3.96	2.55	163.39
LP O 18	σ* O 10 - H 11	9.37	1.62	158.52
Configuration (C)				
LP Cl 8	σ*O 19 - H 25	0.05	2.62	159.39
Configuration (D)				
LP Cl 7	σ*O 15 - H 21	1.02	2.92	154.19
LP O 17	σ*O 10 - H 11	40.55	1.54	162.14
Tetrahedral surface				
Configuration (E)				
LP O 31	σ*O 10 - H 11	3.71	2.24	149.35
Configuration (F)	/	/	/	/

Conclusions

The aim of the present work which lies within the framework of the environmental clean-up, was to show by means of theoretical calculations the process of adsorption of the organic pollutant 2,4,6-trichlorophenol molecule on the kaolinite clay surface in order to identify the sites of adsorption as well as conformations corresponding to the ground state. The fixation of the TCP molecule on the mineral surface depends on its capability to form hydrogen bonds with the surface hydroxyl groups on the octahedral side and with basal oxygen atoms on the tetrahedral side. Various locations and orientations of TCP on the surfaces clay were found but the minimum energy structure corresponds to that where the TCP molecule is adsorbed in position including TCP hydroxyl group and one chlorine atom in the strongest hydrogen bonds. This position seems to minimize repulsive interactions. The hydroxyl group of the TCP molecule has the role of proton acceptor and forms several hydrogen bonds with protons from surface hydroxyl groups: electron donor-acceptor complex between kaolinite surface and TCP molecule were dominant adsorption mechanisms. The results point out a preferential adsorption of TCP on the octahedral surface. From the theoretical predictions of the thermodynamic parameters, it can be concluded that the process is driven thermodynamically.

References

- Austen, K.F., White, T.O.H., Marmier, A., Parker, S.C., Artacho, E. and Dove, M.T. 2008. Electrostatic versus polarization effects in the adsorption of aromatic molecules of varied polarity on insulating hydrophobic surface, *Journal of Physics: Condensed Matter*, 20(3): 35215- 35222.
- Becke, A. D. 1993. Density-functional thermochemistry. III. The role of exact exchange, *Journal of Chemical Physics*, 98(7): 5648-5652.
- Bish, D. L. 1993. Rietveld refinement of the kaolinite structure, *Clays and Clay Minerals*, 41(6): 738-744.
- Boys, S. F. and Bernardi, F. 1970. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, *Molecular Physics*, 19 (4): 553-566.
- Castro, E.A.S., Gargano, R. and Martins, J.B.L. 2012. Benzene–Kaolinite Interaction Properties, *International Journal of Quantum Chemistry*, 112(16): 2828–2831.
- Chaliha, S. and Bhattacharyya, K.G. 2008. Catalytic wet oxidation of 2-chlorophenol, 2, 4-dichlorophenol and 2, 4, 6-trichlorophenol in water with Mn (II)-MCM41, *Chemical Engineering Journal*, 139(3): 575-588.
- Dąbrowski, A., Podkościelny, P., Hubicki, Z. and Barczak, M. 2005. Adsorption of phenolic compounds by activated carbon--a critical review, *Chemosphere*, 58(8): 1049-1070.
- EPA, 1980. Ambient Water Quality for Chlorinated Phenols.
<http://www.epa.gov/ost/pc/ambientwqc/chlorinatedphenols80.pdf>.
- EPA, 2002. Appendix A to 40 CFR: Priority Pollutants. <http://www.epa.gov/region1/npdes/permits/generic/prioritypollutants.pdf>.
- Gao, R. and Wang, J. 2007. Effects of pH and temperature on isotherm parameters of chlorophenols biosorption to anaerobic granular sludge, *Journal of Hazardous Materials*, 145(3): 398-403.
- González, M., Sandra, P. and Bernès, S. 2007. 2,4,6-Trichlorophenol, *Acta Crystallographica: Section E* (Wiley-Blackwell), 63(10): o3947-o3947.
- Guimaraes, J.L., Peralta-Zamora, P. and Wypych, F.1998. Covalent grafting of phenylphosphonate groups onto the interlamellar aluminol surface of kaolinite, *Journal Of Colloid And Interface Science*, 206(1): 281-287.
- Hameed, B.H. 2007. Equilibrium and kinetics studies of 2,4,6-trichlorophenol adsorption onto activated Colloids and Surfaces A: Physicochemical and Engineering Aspects, 307(1-3): 45-52.
- Hameed, B.H., Tan, I.A.W. and Ahmad, A.L. 2009. Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2,4,6- trichlorophenol, *Journal of Hazardous Materials*, 164(2-3): 1316-1324.
- Karelson, M., Lobanov, V.S. and Katritzky, R. 1996. Quantum-Chemical Descriptors in QSAR/QSPR Studies, *Chemical Reviews*, 96 (3): 1027-1044.
- Komori, Y., Sugahara, Y. and Kuroda, K. 1998, A Kaolinite-NMF-Methanol Intercalation Compound as Versatile Intermediate for Further Intercalation Reaction of Kaolinite, *Journal of Materials Research*, 13(4): 930-934.

- Michalkova, A. and Tunega, D. 2007. Kaolinite:Dimethylsulfoxide Intercalate A Theoretical Study, *The Journal of Physical Chemistry - Part C*, 111(30) : 11259-11266.
- Michalkova, A., Robinson T. L. and Leszczynski J. 2011. Adsorption of thymine and uracil on 1 : 1 clay mineral surfaces: comprehensive ab initio study on influence of sodium cation and water. *Physical Chemistry Chemical Physics: PCCP*, 13(17): 7862–7881.
- Ogawa, M. and Kuroda, K. 1995. Photofunctions of intercalation compounds, *Chemical Reviews*, 95(2): 399-438.
- Oh, C.G., Ahn, J.H. and Ihm, S.K. 2003. Adsorptive removal of phenolic compounds by using hypercrosslinked polystyrenic beads with bimodal pore size distribution, *Reactive and Functional Polymers*, 57(2-3): 103-111.
- Patwardhan, S.V. and Clarson, S.J. 2002. Silicification and Biosilification: Part 1. Formation of Silica Structures Utilizing A Cationically Charged Synthetic Polymer At Neutral pH and Under Ambient Conditions. *Polymer Bulletin*, 48(4-5): 367-371.
- Podkoscielny, P., Dabrowski, A. and Marijuk, O.V. 2003. Heterogeneity of active carbons in adsorption of phenol aqueous solutions, *Applied Surface Science*, 205(1): 297-303.
- Polati, S., Gosetti, F., Gianotti, V. and Gennaro, MC. 2006. Sorption and desorption behavior of chloroanilines and chlorophenols on montmorillonite and kaolinite, *Journal of Environmental Science & Health, Part B -- Pesticides, Food Contaminants, & Agricultural Wastes*, 41(6): 765-779.
- Robinson, T.L., Michalkova, A., Gorb, L. and Leszczynski, J. 2007. Hydrogen bonding of thymine and uracil with surface of dickite: An ab initio study, *Journal of Molecular Structure*, 844: 48-58.
- Sainz-Díaz, C.I., Francisco-Márquez, M. and Vivier-Bunge, A. 2011. Adsorption of polyaromatic heterocycles on pyrophyllite surface by means of different theoretical approaches, *Environmental Chemistry*, 8(4): 429-440.
- Salvador, F. and Merchan, M.D. 1996. Study of the desorption of phenol and phenolic-compounds from activated carbon by liquid-phase temperature-programmed desorption, *Carbon*. 34(12): 1543-1551.
- Savin, S.M., Lee, M. 1988. Isotopic Studies of phyllosilicates, in: S.W.Bailey et al., (ed.), by S.W.Bailey, *Hydrous phyllosilicates (exclusive of micas)*, Washington: Mineralogical Society of America, vol.19, pp.189-219.
- Scott, A.M., Burns, E.A. and Hill, F.C. 2014. Theoretical study of adsorption of nitrogen-containing environmental contaminants on kaolinite surfaces, *Journal Of Molecular Modeling*, 20 (8): 2373–2377.
- Song, K.H., Wang, X., Qian, P., Zhang, C. and Zhang, Q. 2013. Theoretical study of interaction of formamide with kaolinite., *Computational and Theoretical Chemistry*, 1020: 72-80.
- Tan, I.A.W., Ahmad, A.L. and Hameed, B.H. 2008. Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology, *Journal of Hazardous Materials*, 153(1): 709-717.
- Tan, I.A.W., Ahmad, A.L. and Hameed, B.H. 2009. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, *Journal of Hazardous Materials*, 164(2-3):473-482.
- Tan, I.A.W., Ahmad, A.L. and Hameed, B.H. 2009. Fixed-bed adsorption performance of oil palm shell-based activated carbon for removal of 2,4,6-trichlorophenol, *Bioresource technology*, 100(3): 1494–1496.
- Tunney, J.J. and Detellier, C. 1996. Aluminosilicate Nanocomposite Materials. Poly(ethylene glycol)-Kaolinite Intercalates, *Chemistry of Materials*, 8(4): 927-935.
- Tzou, Y.M., Wang, S.L., Liu, J.C., Huang, Y. and Chen, J.H. 2008. Removal of 2,4,6-trichlorophenol from a solution by humic acids repeatedly extracted from a peat soil, *Journal of Hazardous Materials*, 152(2): 812-819.
- Vidic, R.D., Suidan, M.T. and Brenner, R.C. 1993. Oxidative Coupling of Phenols on Activated Carbon – Impact on Adsorption Equilibrium, *Environmental Science and Technology*, 27(10): 2079-2085.
- Wang, X., Qian, P., Song, K., Zhang, C. and Dong, J. 2013. The DFT Study of Adsorption of 2,4-Dinitrotoluene on Kaolinite Surfaces, *Computational and Theoretical Chemistry*, 1025: 16-23.
- Wang, X.P., Shan, X.Q., Luo, L., Zhang, S.Z. and Wen, B. 2005. Sorption of 2,4,6-trichlorophenol in model humic acid-clay systems *Journal of agricultural and food chemistry*, 53(9): 3548-3555.